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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR Hereby <b>09/647650</b>	
INTERNATIONAL APPLICATION NO. <b>PCT/FR99/00748</b>		INTERNATIONAL FILING DATE <b>03/31/99</b>		PRIORITY DATE CLAIMED <b>04/03/98</b>	
TITLE OF INVENTION <b>PHOTOCATALYTIC COMPOSITION</b>					
APPLICANT(S) FOR DO/EO/US <b>ESCAFFRE, Pascale; GIRARD, Pierre; DUSSAUD, Joseph ; BOUVIER, Leonie</b>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</li> <li>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2))             <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li>7. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> <li>8. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))             <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> have been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>9. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>10. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li>11. <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li>12. <input checked="" type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> </ol>					
<b>Items 13 to 20 below concern document(s) or information included:</b>					
<ol style="list-style-type: none"> <li>13. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>14. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>15. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li>16. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>17. <input type="checkbox"/> A substitute specification.</li> <li>18. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>19. <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail</li> <li>20. <input checked="" type="checkbox"/> Other items or information:</li> </ol>					
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## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Escaffre et al.

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Group Art Unit: Not assigned

Filed: Herewith

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Title: PHOTOCATALYTIC COMPOSITION

To: Assistant Commissioner for Patents  
Box PATENT APPLICATION  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

Dear Sir:

Prior to examination, please amend the application as follows:

**In the Claims:**

Please delete claims 12, 22 and 23.

Please amend claims 1-11 and 13-21 as set forth below.

1. (Amended) A photocatalytic composition comprising at least one photocatalyzing agent and at least one inorganic binder, [characterized in that] wherein the inorganic binder comprises an aqueous colloidal dispersion [of silicon dioxide ( $\text{SiO}_2$ ), in which the  $\text{SiO}_2$  particles represent] comprising from 20 to 50% by weight [of the colloidal aqueous dispersion and have] silica particles having a diameter of between 10 and 40 nanometers, said silica particles being capable of bonding together after having coated the photocatalyzing agent.

2. (Amended) The photocatalytic composition as claimed in claim 1, [characterized in that] wherein the binding agent consists [exclusively] essentially of an aqueous colloidal dispersion of [silicon dioxide ( $\text{SiO}_2$ )] silica.
3. (Amended) The photocatalytic composition as claimed in claim 1, [characterized in that] wherein the photocatalyzing agent is anatase  $\text{TiO}_2$ .
4. (Amended) The photocatalytic composition as claimed in claim 3, [characterized in that] wherein the diameter of the  $\text{TiO}_2$  particles is between 10 and 30 nanometers.
5. (Amended) The photocatalytic composition as claimed in claim 3, [characterized in that] comprising from 10 to 60 parts (as dry matter) of the aqueous colloidal dispersion of [silicon dioxide] silica, the balance to 100 parts consisting of  $\text{TiO}_2$ .
6. (Amended) The photocatalytic composition as claimed in claim 5, [characterized in that it comprises] comprising 50 parts of titanium dioxide and 50 parts of the aqueous colloidal dispersion of [silicon dioxide] silica.
7. (Amended) The photocatalytic composition [as claimed in claimed in one of] according to claim 1, [characterized in that it furthermore includes] additionally comprising zeolites modified by metal ions capable of preventing the development of undesirable microorganisms and fungi.
8. (Amended) The photocatalytic composition as claimed in claim 1, [characterized in that it furthermore includes] additionally comprising active carbon.
9. (Amended) A process for manufacturing a photocatalytic composition as claimed in claim 1, [characterized in that, while stirring,] comprising mixing the

photocatalyzing agent [is mixed] into the inorganic binder while stirring until a homogeneous suspension is obtained.

10. (Amended) A process for manufacturing a photocatalytic composition as claimed in claim 7, [characterized in that, while stirring,] comprising mixing the photocatalyzing agent and the zeolites modified by metal ions [are mixed] while stirring into the inorganic binder until a homogeneous suspension is obtained.

11. (Amended) A process for manufacturing a photocatalytic composition as claimed in claim 8, [characterized in that, while stirring,] comprising mixing the photocatalyzing agent and the active carbon [are mixed] while stirring so as to obtain a homogeneous suspension.

13. (Amended) A filtering medium comprising a support [coated on] having at least one [of its faces] surface coated with a layer [of] comprising the photocatalytic composition as claimed in claim 1.

14. (Amended) The filtering medium as claimed in claim 13, [characterized in that] wherein the support is a fibrous support.

15. (Amended) The filtering medium as claimed in claim 13, [characterized in that] wherein the support is an acoustic panel.

16. (Amended) The filtering medium as claimed in claim 13, [characterized in that when one of the faces of the support is coated with said photocatalytic composition, the other face] wherein a second surface of the support is coated with a second composition capable of eliminating odors, the second composition comprising a derivative of undecylenic acid.

17. (Amended) The filtering medium as claimed in claim 16, [characterized in that] wherein said second composition [furthermore includes] additionally comprises dioctyl sulfosuccinate capable of destroying mite-type insects.

18. (Amended) The filtering medium as claimed in claim 13, [characterized in that it furthermore includes] additionally comprising a prefilter [in the form of] comprising a support coated with [said] a second composition capable of eliminating odors, the second composition comprising a derivative of undecylenic acid.

19. (Amended) The filtering medium as claimed in claim 18, [characterized in that] wherein said second composition [furthermore includes] additionally comprises dioctyl sulfosuccinate capable of destroying mite-type insects.

20. (Amended) A process for manufacturing a filtering medium as claimed in claim 13, [characterized in that] wherein the support is coated with the photocatalytic composition [as claimed in one of claims 1 to 8] in an amount ranging from 5 to 40 g/m<sup>2</sup> of TiO<sub>2</sub>.

21. (Amended) A process for manufacturing a filtering medium as claimed in [claims] claim 6 [or 18], [characterized in that] wherein said second composition is coated in an amount of 2 g/m<sup>2</sup> on the support.

Please add claims 24-27 as follows:

24. (New) A method for treating a fluid containing organic pollutants, said method comprising:

providing a photocatalytic composition according to claim 1;

coating the photocatalytic composition on a support;

contacting the coated support with the fluid containing organic pollutants;  
and  
exposing the coated support to ultraviolet radiation;  
whereby organic pollutants contained in the fluid are degraded to carbon dioxide.

25. (New) A method according to claim 24 wherein the fluid is air.

26. (New) A method according to claim 24 wherein the fluid is a liquid effluent.

27. (New) A method according to claim 24 wherein the support is a fibrous support.

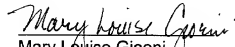
28. (New) A method according to claim 24 wherein the support is an acoustic panel.

### REMARKS

Claims 1-23, as amended, are pending in International Application WO 99/51345, which claims priority from French patent application 98.04401, filed April 3, 1998. The claims are amended herewith in order to bring the form thereof into compliance with the requirements of the U.S. Patent and Trademark Office and U.S. patent law and to clarify what is being claimed. New claims 24-27 relate to matter contained in canceled claims 12, 22 and 23. No new matter has been added.

Should any questions arise in connection with this Application, Applicants' Attorney can be reached at the below-listed telephone number.

Respectfully submitted,

  
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Dated: October 3, 2000

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PHOTOCATALYTIC COMPOSITION

5           The invention relates to a novel photocatalytic composition, to its manufacturing process and to its use.

          It also relates to a filtering medium covered with this photocatalytic composition, as well as to its  
10   manufacturing process and to its use.

          In the rest of the description and in the claims, the term "photocatalytic agent" denotes an agent capable of destroying the various organic pollutants present in the air or in water, by a  
15   photochemical reaction caused by ultraviolet (UV) irradiation. This chemical reaction is known widely by the term "photocatalytics" and is used for the treatment of air or water.

          Schematically, the photocatalytic reaction is  
20   initiated by activating a semiconductor solid by UV radiation at a wavelength of less than 380 nanometers, causing electronic changes within the semiconductor and resulting, in the presence of air or water, in the creation of oxygen-containing radicals at the surface  
25   of the semiconductor. These radicals attack the organic compounds adsorbed on the semiconductor and, by a succession of chemical reactions involving the oxygen in the air or water, degrade the organic compounds until the carbon of the carbon chains is completely  
30   converted into carbon dioxide (CO<sub>2</sub>).

          The photocatalytic reaction is able to convert, via the process described above, a large number of pollutants in the air, and especially NO<sub>x</sub>, NH<sub>3</sub>, H<sub>2</sub>S, CO, O<sub>3</sub>, chlorinated or nonchlorinated C<sub>2</sub>-C<sub>4</sub> alkenes,  
35   chloromethane, iso-octane, benzene, toluene, xylene, isopropylbenzene, C<sub>1</sub>-C<sub>4</sub> saturated aliphatic alcohols, methyl mercaptane, chlorophenol, nitrophenol, methyl tert-butyl ether, dimethoxymethane, C<sub>1</sub>-C<sub>4</sub> aldehydes,

acetone, formic acid, acetic acid, 2-methylpropanoic acid, dichloroacetyl chloride, dimethylformamide, trimethylamine, acetonitrile and pyridine.

In practice, anatase titanium dioxide  $\text{TiO}_2$  is used as the semiconductor solid, that is to say as the photocatalyzing agent, which titanium dioxide, activated by UV light, is electronically modified so as to lead to the formation of hydroxyl radicals  $\text{OH}^\bullet$  and oxygen radicals  $\text{O}^\bullet$  capable of attacking the organic compounds adsorbed on the  $\text{TiO}_2$  by degrading them until the organic carbon is completely converted into carbon dioxide.

However, it is possible to use other photocatalyzing agents such as, for example, those chosen from the group of metal oxides, alkaline-earth oxides, actinide oxides and rare-earth oxides.

For the treatment of air and of liquid effluents, it is necessary to fix the photocatalytic compositions by means of binding agents onto supports, especially fibrous supports or glass-fiber supports. In the rest of the description and in the claims, this "photocatalytic composition/support" combination is referred to by the term "filtering medium".

It was proposed a long time ago to use, as the binding agent, organic molecules of the type comprising polyvinyl acetate, polyvinyl alcohol, etc.

It has rapidly been found that this use could not be satisfactory if the carbon chains of the binder are also subjected to the photocatalysis process and are therefore degraded, so that the lifetime of the composition would be limited thereby.

To solve this problem, various techniques have been proposed, consisting in removing the carbon from the binder by calcining, especially the technique of fixing the catalyst by PMTP (Previously Made Titanium Powder) or else by CVD (Chemical Vapor Deposition), these techniques being described in particular in the

Journal "CATALYSIS TODAY", Vol. 39, No. 3, Pages 221 and 222.

5 However, this type of technique has a number of drawbacks, such as that of increasing the duration and the cost of preparing the composition. Furthermore, and above all, the calcining carried out at temperatures of about 1700°C results in the formation of a powder which makes the composition difficult to use.

10 To solve this problem, it has been proposed, in document FR-A-2 749 777, to replace the organic binder with an inorganic binder consisting of an inorganic aluminosilicate polymer, of the imogolite type.

15 The photocatalytic composition described in that document is in the form of an aluminosilicate gel to which a colloidal solution of a photocatalyzing agent is added. The time required to prepare the aluminosilicate gel is of the order of a few days and requires a multitude of relatively complicated steps. A thixotropic gel transparent to solar radiation is  
20 obtained, which has to be fluidized by agitation in order to allow uniform coating on a support.

More specifically, in order to manufacture a filtering medium, the gel obtained is applied to a support and then dried using an unspecified technique.  
25 The various trials show that, depending on the light source used, only about 12 or 26% of the pollutants are destroyed (see Example 3).

Although the photocatalytic composition described in that document has the advantage of being  
30 able to be coated on a support as a single layer, the preparation of the composition is not only very complicated but it also leads to inadequate results.

To solve this problem, it has been proposed, in documents JP-A-09/171801 and WO-A-97/00134, to coat the  
35 photocatalytic composition as such on a support, via an adhesive layer. The adhesive layer consists of a resin which may comprise, in certain embodiments, from 5 to 40% by weight of colloidal silica.

In other words, this solution has the drawback, on the one hand, of increasing the number of steps needed to manufacture a filtering medium (coating of two successive layers on the support), and, on the other hand, of using resins, which are by definition organic, which can be consumed during the photocatalysis process.

One of the problems that the invention aims to solve is that of providing a photocatalytic composition which is simple to prepare from commercially available constituents and is capable of being coated directly on a support.

Another problem that the invention aims to solve is to improve the adsorptivity and the photocatalytic effectiveness, that is to say the efficiency of the photocatalyzing agent.

To solve the problem of providing a composition simple to use and capable of being applied to a substrate as a single layer, the invention proposes a photocatalytic composition comprising at least one photocatalyzing agent and at least one inorganic binding agent, characterized in that the inorganic binding agent comprises an aqueous colloidal dispersion of silicon dioxide ( $\text{SiO}_2$ ), said aqueous colloidal dispersion of silicon oxide comprising silica particles capable of bonding together after having coated the photocatalyzing agent.

"Aqueous colloidal dispersion of silicon dioxide ( $\text{SiO}_2$ )" should be understood to mean a negatively charged dispersion of amorphous silica particles, of high specific surface area, in water. In practice, the specific surface area of the silica particles is greater than  $80 \text{ m}^2/\text{g}$ , advantageously  $100 \text{ m}^2/\text{g}$ , for a particle size of between 25 and 30 nanometers. Likewise, it is greater than  $300 \text{ m}^2/\text{g}$ , advantageously  $350 \text{ m}^2/\text{g}$ , for a particle size of between 4 and 6 nanometers. On their surface, the silica particles have OH groups and  $\text{OH}^-$  ions which form an

electric double layer, thus giving said particles self-bonding properties. As already stated, the silica particles are capable of bonding together after having coated the particles of photocatalyzing agents.

5 To solve the problem of how to improve the adsorbitivity and the photocatalytic effectiveness of the composition, the binding agent consists exclusively of an aqueous colloidal dispersion of silicon dioxide ( $\text{SiO}_2$ ).

10 It seems in fact quite surprising that the use of an aqueous colloidal dispersion of  $\text{SiO}_2$  of the type described above makes it possible to significantly improve the degree of adsorption of the polluting substances on the photocatalyzing agent as well as the efficiency of the photocatalysis, this being probably  
15 due to the self-bonding properties of the  $\text{SiO}_2$  particles.

According to a first characteristic of the invention, the  $\text{SiO}_2$  particles represent from 20 to 50%  
20 by weight, advantageously 48% by weight, of the colloidal aqueous dispersion.

For a concentration of less than 20%, the photocatalyzing agent is less resistant to rubbing and is transformed into a powder.

25 For a concentration of greater than 50%, the photocatalyzing agent loses its activity.

According to another characteristic of the invention, the silicon dioxide particles forming the aqueous dispersion have a diameter of between 10 and  
30 50 nanometers, advantageously between 20 and 30 nanometers.

Advantageously, anatase titanium dioxide ( $\text{TiO}_2$ ) alone is used as the photocatalyzing agent.

35 However, the photocatalyzing agent may also result from mixing several agents, such as  $\text{TiO}_2$ , cerium oxide, etc.

To improve the photocatalytic effectiveness, the titanium dioxide ( $\text{TiO}_2$ ) particles have a diameter of between 10 and 30 nanometers.

Likewise, to obtain optimum adsorption effectiveness, the photocatalytic composition comprises from 10 to 60 parts (as dry matter) of the aqueous colloidal dispersion of silicon dioxide, the balance to 100 parts consisting of anatase  $\text{TiO}_2$ .

Advantageously, the photocatalytic composition comprises 50 parts of the aqueous colloidal dispersion of silicon dioxide and 50 parts of anatase titanium dioxide.

According to another embodiment of the invention, so as to prevent the development of undesirable microorganisms and fungi contained in the ambient air, the photocatalytic composition furthermore comprises zeolites modified by metal ions.

The term "zeolites" denotes a group of natural hydrated aluminosilicates of alkali or alkaline-earth metals.

In practice, the metal ions are chosen from the group comprising silver, copper and zinc and are used in an amount from 1 to 3%. Advantageously, the zeolite is modified with 1.5% of silver ions.

It has in fact been found that this type of composition makes it possible to accelerate the destruction of the microorganisms and fungi contained in the ambient air while still destroying the organic pollutants giving rise to certain odors, by combining the properties of the modified zeolites with those of the photocatalysis described above.

According to an advantageous embodiment of the invention, the photocatalytic composition consists (by weight) of :

- 30 to 50%, advantageously 47%,  $\text{SiO}_2$ ,
- 30 to 50%, advantageously 47%, anatase  $\text{TiO}_2$ ,
- 2 to 10%, advantageously 6%, zeolite containing 2% silver.

According to another embodiment of the invention, so as to adsorb the organic molecules present in the pollution peaks, the photocatalytic composition furthermore includes active carbon.

5 In a known manner, the active carbon is present in the form of fibers or particles having a high specific surface area and thus allowing the organic molecules to be adsorbed.

Consequently, the photocatalytic composition, 10 by including active carbon, will act on the ambient air in two stages,

u firstly, adsorption of the polluting agents present in the pollution peaks on the active carbon;

15 u then, photocatalysis degrading the pollutant contained in the active carbon, thus allowing said active carbon to be regenerated.

In other words, the lifetime of this composition will be greatly increased over the lifetime 20 of the active carbon alone.

According to one advantageous version of this embodiment, the photocatalytic composition consists (by weight) of :

- 25 u 10 to 40%, advantageously 25%, anatase  $\text{TiO}_2$ ;  
u 10 to 40%, advantageously 25%, active carbon;  
u 40 to 60%, advantageously 50%,  $\text{SiO}_2$ .

The invention also relates to the process for manufacturing the photocatalytic composition according to which process, while stirring, the photocatalyzing 30 agent and, where appropriate, the metal-ion-modified zeolites and/or active carbon are introduced into the colloidal aqueous siliceous suspension until a homogeneous suspension able to be applied directly to a support is obtained.

35 The invention therefore relates to the use of the photocatalytic composition in paint form.

The invention also relates to a filtering medium. As already stated, the expression "filtering

medium" denotes the combination of a support and a photocatalytic composition. In a known manner, a filtering medium may be composed of one or more treated supports.

5 Thus, the photocatalytic composition of the invention may be deposited on at least one of the faces of a support. It has in fact been found that, by virtue of their self-bonding properties, the  $\text{SiO}_2$  particles not only bond together, while coating the  $\text{TiO}_2$  particles, but also bond to the support. Furthermore, 10 and above all, a large increase in the efficiency of the photocatalysis is observed, this probably being due to the particular structure of the  $\text{SiO}_2$  particles, which makes it possible to maintain a high porosity and a 15 high specific surface area of the layer after drying.

Unlike the coating of a composition transparent to UV radiation described in document FR-A-2,749,777, the coating produced from the composition of the invention is opaque to UV radiation while maintaining 20 optimum efficiency, which property may be used in fields of application of the type comprising displays, banners and wall papers.

Moreover, it is possible to use several types of supports, such as glass fibers or a nonwoven 25 support, this been so in a nonlimiting manner.

In another embodiment, the support is in the form of an acoustic panel.

The term "acoustic panel" denotes in particular the tiles making up false ceilings.

30 In practice, the tile is coated with the photocatalytic composition.

Natural convection produces a movement of cold air from the bottom of the room which, while being heated, rises to the top of the room and thus comes 35 into contact with the tiles making up the ceiling which, under the action of incandescent light or daylight, trigger a photocatalytic reaction resulting in the destruction of the gasses.



The support may also be an organic fibrous support of the paper type. It has in fact been found that the use of an aqueous colloidal dispersion of  $\text{SiO}_2$  makes it possible to coat the organic fibers of the support so that said support is not exposed to the photocatalysis reaction and therefore does not deteriorate over time.

The use of the colloidal dispersion of  $\text{SiO}_2$  on this type of support therefore makes it possible to increase the lifetime of the filtering medium.

According to an advantageous embodiment of the invention, only one face of the support of the filtering medium is coated with the photocatalytic composition of the invention, the other face being coated with a second composition capable of eliminating odors, comprising a derivative of undecylenic acid.

Advantageously, the derivative of undecylenic acid is sodium undecylenate or else methyl or ethyl undecylenate, this being so in a nonlimiting manner.

In order to destroy insects of the mite type, said second composition also includes dioctyl sulfosuccinate.

It has in fact being found that this type of composition makes it possible to combine and derive benefit from several different actions, namely:

- that of the undecylenic acid derivative which eliminates the odors, especially of the type comprising amines, sulfur derivatives etc.
- that of dioctyl sulfosuccinate which acts by destroying the keratin of mites.

In practice, said second composition contains, (by dry weight):

- from 80 to 98%, advantageously 96%, sodium undecylenate;
- from 2 to 20%, advantageously 4%, dioctyl sulfosuccinate.

In a variant, apart from a support coated with the photocatalytic composition, the filtering medium

includes a prefilter in the form of a support coated with a composition capable of eliminating odors and destroying mite-type insects, comprising a derivative of undecylenic acid and of dioctyl sulfosuccinate.

5       The invention also relates to the process for manufacturing a filtering medium comprising a support on which the photocatalytic composition of the invention is coated in an amount from 5 to 40 g/m<sup>2</sup>, advantageously 20 g/m<sup>2</sup>, of TiO<sub>2</sub>.

10       For a value of less than 5 g/m<sup>2</sup>, the photocatalysis reaction is reduced on account of the too small a thickness of the layer of the photocatalytic composition on the support.

15       For a value greater than 40 g/m<sup>2</sup> no increase in the photocatalytic efficiency is observed.

20       In the embodiment in which the filtering medium has a support face or a prefilter coated with a composition based on undecylenic acid and on a sulfosuccinate, this coating is produced in an amount of 2 g/m<sup>2</sup>.

25       Furthermore, the process for manufacturing the filtering medium of the invention has the advantage of being able to be carried out continuously, it being possible for the coating to be produced in particular on a size press, or any other conventional impregnation or coating process, thereby making the process very simple compared with the prior art.

30       In the case of wallpapers or acoustic panels, the composition of the invention may be in the form of a paint to be applied directly to the support.

      These filtering media can therefore be used for the treatment and the purification of air, but also for the treatment of liquid effluents.

35       The invention and the advantages which stem therefrom will become more apparent from the following illustrative examples supported by the appended Figure 1, which shows the reaction efficiency of the

photocatalytic composition forming the subject of the invention.

Example 1

5           The following experiment shows the improvement in the adsorptivity and the photocatalytic efficiency of the photocatalytic composition of the invention compared with a filter medium of the prior art.

10           The test consists in immersing a support disk coated with a photocatalytic composition in an isopropyl alcohol solution and then exposing the disk to the action of ultraviolet radiation having a wavelength of less than 380 nanometers for 90 minutes. Under the effect of UV radiation, some of the isopropyl  
15           alcohol is converted into acetone and thus shows the photocatalytic efficiency of the titanium dioxide.

          The disk consists of a fibrous support coated with a photocatalytic composition consisting of:

- 50 parts of binders
- 20           • 50 parts of  $\text{TiO}_2$ .

          Examples 1, 2, 3 and 4 are produced using various types of  $\text{TiO}_2$  coated in an amount from 4.5 to 17 g/m<sup>2</sup> on the disk, which has a surface area of 18 cm<sup>2</sup>. The inorganic binder used is a colloidal dispersion of  
25            $\text{SiO}_2$  sold by Nissan under the trademark "SNOWTEX 50".

          Example 5 uses a filtering medium sold by Matrix, in which the bonding of the  $\text{TiO}_2$  to the support is achieved by calcining the binding agent. The analyses were carried out by gas chromatography.

30           The results are given in the following table:

TABLE 1

	Example 1 TiO <sub>2</sub> DTS1 <sup>1</sup> 16 g/m <sup>2</sup>	Example 2 TiO <sub>2</sub> REF2 <sup>2</sup> 17 g/m <sup>2</sup>	Example 3 TiO <sub>2</sub> REF2 4.5 g/m <sup>2</sup>	Example 4 TiO <sub>2</sub> P-25 <sup>3</sup> 12.5 g/m <sup>2</sup>	Example 5 Filtering medium Prior art <sup>4</sup> 2.88 g/m <sup>2</sup>
Amount of acetone formed/ μmol	46	69	50	71	26.5

1. DT 51<sup>®</sup> : TiO<sub>2</sub> sold by Rhodia
2. REF2 : TiO<sub>2</sub> having a specific surface area of 75 m<sup>2</sup>/g
3. Sold by Degussa
4. Sold by Matrix.

It may be seen that the last disk causes a very small amount of acetone to be formed compared with the photocatalytic composition of the invention. It was also found that a TiO<sub>2</sub> coating of between 4.5 g/m<sup>2</sup> and 12.5 g/m<sup>2</sup> (Examples 3 and 4) makes it possible to obtain a high photocatalytic efficiency.

Example 2

The reaction efficiency was calculated for various compositions according to the invention coated on a support of the nonwoven type (reference 1045) manufactured by Ahlstrom Lystil and perforated by the PERFOJET process so as to improve the through-flow (low pressure drop). The pollutant used is isobutane.

The composition contains two types of TiO<sub>2</sub>, differing in specific surface area, namely 250 m<sup>2</sup>/g (REF 1) and 75 m<sup>2</sup>/g (REF 2), respectively.

All the essential parameters have been shown in the following table, namely the proportions of each of the constituents, the area irradiated, the irradiation time and the average reaction efficiency, and the

5 amount of  $\text{TiO}_2$  deposited, 10 or 20  $\text{g/m}^2$  (REF 1 or REF 2).

TABLE 2

	Binder*/TiO <sub>2</sub> in parts as dry matter	Area (cm <sup>2</sup> )	Irradiation time (h)	Average reaction efficiency (%)
1A REF 1 10 g/m <sup>2</sup>	20/80	64.5	6	54.30
		65.8	6	
		65.8	6	
1B REF 2 10 g/m <sup>2</sup>	20/80	67.4	6	75.38
		67.5	6	
		65.7	6	
1C REF 2 20 g/m <sup>2</sup>	20/80	65.2	6	75.50
		65.4	6	
		65.7	6	
2A REF 1 10 g/m <sup>2</sup>	50/50	64.5	6	44.58
		64.8	6	
		68.2	6	
2A' REF 1 10 g/m <sup>2</sup>	50/50	67.8	5	36.40
		67.8	5	
		67.8	5	
2B REF 2 10 g/m <sup>2</sup>	50/50	66.2	6	88.52
		65.1	6	
		65.1	6	
2B' REF 2 10 g/m <sup>2</sup>	50/50	67.8	5	64.75
		67.8	5	
		67.8	5	
2C REF 2 20 g/m <sup>2</sup>	50/50	66.2	6	81.53
		66.2	6	
		66.4	6	
3B REF 2 10 g/m <sup>2</sup>	50/50	67.2	6	84.03
		67.2	6	
		67.2	6	
4B REF 2 10 g/m <sup>2</sup>	50/50	66.9	6	2.95
		64.8	6	
		66.9	6	
No C4H10				

\*SNOWTEX 50 sold by Nissan.

It may be seen that the best reaction efficiencies are obtained for compositions of the invention containing 50 parts of the colloidal aqueous dispersion of silica ( $\text{SiO}_2$ ) and 50 parts of titanium dioxide REF 2.

It should also be noted that 10 g/m<sup>2</sup> coatings of  $\text{TiO}_2$  result in reaction efficiencies that are higher than in 20 g/m<sup>2</sup> coatings, all other conditions being the same, thereby reducing the cost of the filtering media.

When the trial is carried out without the isobutane organic pollutant, the photocatalytic efficiency is virtually zero, which is logical. It may be estimated that the low value obtained in this case (2.95%) corresponds to the decomposition of parasitic organic matter. The numbers in the table are therefore significant to within 3%.

The appended Figure 1 shows the reaction efficiency obtained for photocatalytic  $\text{TiO}_2$  compositions coated in an amount of 10 g/m<sup>2</sup> i.e. Examples 1A, 1B, 2A, 2A', 2B, 2B', 3B and 4B.

### 25 Example 3

In this example, the efficiency of the photocatalytic composition of the invention including active carbon was evaluated.

To do this, a photocatalytic composition is coated on a nonwoven-type support (Reference 1045) manufactured by Ahlstrom Lystil and perforated by the PERFOJET process.

The photocatalytic composition consists of:

- 35     v 25%  $\text{TiO}_2$  having a specific surface area of 250 m<sup>2</sup>/g
- v 25% active carbon having a specific surface area of 900 m<sup>2</sup>/g, sold by CECA
- v 50% by weight  $\text{SiO}_2$  (SNOWTEX 50).

The medium is irradiated with methanol at a rate of 3.4 ml/minute, the pollutant content being equal to 281 ppm, with or without a saturation phase in the dark.

- 5 The results obtained at equilibrium under UV are identical whether or not the medium has been saturated.

The following were obtained:

- 10 v an amount of methanol equal to 22.3 micromole per hour and per gram;  
v an amount of carbon dioxide (CO<sub>2</sub>) equal to 8.65 micromole per hour and per gram.

- 15 The percentage of mineralization, that is to say of conversion of the polluting agent into CO<sub>2</sub> is 30%.

The carbon balance, resulting from the degradation of methanol into a volatile byproduct, is equal to 56%.

- 20 The advantages of the invention are clearly apparent from the description. In particular, the high adsorptivity and the remarkable efficiency of the TiO<sub>2</sub> when it is in a mixture with a colloidal aqueous dispersion of silica should be noted.

- 25 The simplification of the process for manufacturing the filtering medium, especially using continuous impregnation or coating, especially size-press, techniques, should also be noted.



15-03-2000

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CLAIMS

1. A photocatalytic composition comprising at least one photocatalyzing agent and at least one  
5 inorganic binder, characterized in that the inorganic binder comprises an aqueous colloidal dispersion of silicon dioxide ( $\text{SiO}_2$ ), in which the  $\text{SiO}_2$  particles represent from 20 to 50% by weight of the colloidal aqueous dispersion and have a diameter of between 10  
10 and 40 nanometers, said silica particles being capable of bonding together after having coated the photocatalyzing agent.
2. The photocatalytic composition as claimed in claim 1, characterized in that the binding agent  
15 consists exclusively of an aqueous colloidal dispersion of silicon dioxide ( $\text{SiO}_2$ ).
3. The photocatalytic composition as claimed in claim 1, characterized in that the photocatalyzing agent is anatase  $\text{TiO}_2$ .
- 20 4. The photocatalytic composition as claimed in claim 3, characterized in that the diameter of the  $\text{TiO}_2$  particles is between 10 and 30 nanometers.
5. The photocatalytic composition as claimed in claim 1, characterized in that it comprises from 10 to  
25 60 parts (as dry matter) of the aqueous colloidal dispersion of silicon dioxide, the balance to 100 parts consisting of  $\text{TiO}_2$ .
6. The photocatalytic composition as claimed in claim 5, characterized in that it comprises 50 parts of  
30 titanium dioxide and 50 parts of the aqueous colloidal dispersion of silicon dioxide.
7. The photocatalytic composition as claimed in claim 1, characterized in that it furthermore includes zeolites modified by metal ions  
35 capable of preventing the development of undesirable microorganisms and fungi.

8. The photocatalytic composition as claimed in claims 1, characterized in that it furthermore includes active carbon.

9. A process for manufacturing a photocatalytic composition as claimed in claim 1, characterized in that, while stirring, the photocatalyzing agent is mixed into the inorganic binder until a homogeneous suspension is obtained.

10. A process for manufacturing a photocatalytic composition as claimed in claim 7, characterized in that, while stirring, the photocatalyzing agent and the zeolites modified by metal ions are mixed into the inorganic binder until a homogeneous suspension is obtained.

11. A process for manufacturing a photocatalytic composition as claimed in claim 8, characterized in that, while stirring, the photocatalyzing agent and the active carbon are mixed so as to obtain a homogeneous suspension.

12. Use of the photocatalytic composition according to claim 1 in the form of paint.

13. A filtering medium comprising a support coated on at least one of its faces with a layer of the photocatalytic composition as claimed in claim 1.

14. The filtering medium as claimed in claim 13, characterized in that the support is a fibrous support.

15. The filtering medium as claimed in claim 13, characterized in that the support is an acoustic panel.

16. The filtering medium as claimed in claim 13, characterized in that when one of the faces of the support is coated with said photocatalytic composition, the other face of the support is coated with a second composition capable of eliminating odors, comprising a derivative of undecylenic acid.

17. The filtering medium as claimed in claim 16, characterized in that said second composition furthermore includes dioctyl sulfosuccinate capable of destroying mite-type insects.

5 18. The filtering medium as claimed in claim 13, characterized in that it furthermore includes a prefilter in the form of a support coated with said second composition capable of eliminating odors, comprising a derivative of undecylenic acid.

10 19. The filtering medium as claimed in claim 18, characterized in that said second composition furthermore includes dioctyl sulfursuccinate capable of destroying mite-type insects.

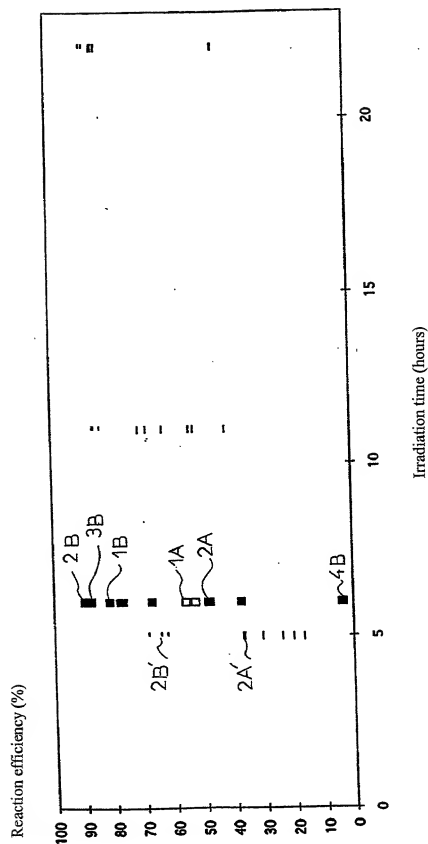
15 20. A process for manufacturing a filtering medium as claimed in claim 13, characterized in that the support is coated with the photocatalytic composition as claimed in one of claims 1 to 8 in an amount from 5 to 40 g/m<sup>2</sup> of TiO<sub>2</sub>.

20 21. A process for manufacturing a filtering medium as claimed in claims 6 or 18, characterized in that said second composition is coated in an amount of 2 g/m<sup>2</sup> on the support.

22. The use of a filtering medium as claimed in claim 13, for the treatment of air.

25 23. Use of a filtering medium as claimed in claim 13, for the treatment of liquid effluents.

FIG 1



Docket No.

## Declaration and Power of Attorney For Patent Application

### English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

#### PHOTOCATALYTIC COMPOSITION

the specification of which

(check one)

☒ is attached hereto.

☐ was filed on \_\_\_\_\_ as United States Application No. or PCT International

Application Number \_\_\_\_\_

and was amended on \_\_\_\_\_

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

FR 98.04401	FRANCE	03/04/98	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
PCT/FR 99/00748	WO	31/03/99	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
			<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)  
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)  
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)  
(patented, pending, abandoned)


I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

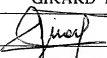
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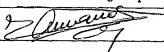
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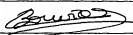
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